



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 13/16, C11D 17/00, 3/37, 3/386	A1	(11) International Publication Number: WO 97/24178 (43) International Publication Date: 10 July 1997 (10.07.97)
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(54) Title: POLYMERIC PARTICULATE MATERIALS AND COMPOSITIONS CONTAINING THEM (57) Abstract <p>Particle having a polymeric matrix which includes an enzyme or other detergency active ingredient and which is formed of a copolymer of (a) an ethylenically unsaturated hydrophobic monomer with (b) a free base monomer of the formula: $\text{CH}_2 = \text{CR}^1\text{COXR}^2\text{NR}^3\text{R}^4$ where R is hydrogen or methyl, R^2 is alkylene containing at least two carbon atoms, X is O or NH, R^3 is a hydrocarbon group containing at least 4 carbon atoms and R^4 is hydrogen or a hydrocarbon group.</p>		

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POLYMERIC PARTICULATE MATERIALS
AND COMPOSITIONS CONTAINING THEM

5 This invention relates to liquid detergents and to particulate materials which can contain detergent active ingredients and which can be utilised for introducing the active ingredients into a liquid detergent. In particular the invention relates to compositions wherein the active ingredient is a detergent enzyme.

10 We have described in EP 356239 certain compositions which are intended to promote the maintenance of enzymatic activity of enzyme incorporated into a liquid detergent and we describe, inter alia, the provision of particles having a core (and optionally an outer polymeric shell) of a
15 matrix polymer through which the enzyme is distributed. It is stated that the polymer can be a synthetic polymer formed from an ethylenically unsaturated water soluble monomer or monomer blend which may be non-ionic or ionic, and it is mentioned that dimethyl amino ethyl (meth)
20 acrylate can be used as a suitable cationic monomer. The preferred polymer is based on 0%-50% acrylamide and 50%-100% acrylic acid or soluble salt thereof. It is also stated that the polymer can be a polymer which is insoluble in water but is soluble or swellable in alkali, the
25 monomers being a blend of anionic monomer and ethylenically unsaturated non-ionic monomer, for example, styrene.

In WO92/20771 we described that the protection of enzyme can be improved if there is a layer of hydrophobic oil between the matrix polymer core and the outer shell of
30 polymer and if the matrix is sufficiently hydrophobic that it will partition preferentially into the oil rather than the water. It is mentioned that the preferred polymers are co-polymers of ionic monomers with hydrophobic monomers, such as styrene, and can be made by solution polymerisation
35 in organic solvent or by oil-in-water emulsion polymerisation. It is stated that the ionic monomer can be an amino-polymer which can be present initially as a water

soluble salt but can be insolubilised by conversion to the free base. Thus we describe a matrix which is formed of a water-insoluble hydrophobic polymer which contains recurring units of hydrophobic water-insoluble monomer and
5 of cationic monomer having amino groups in free base form.

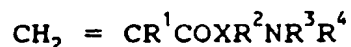
This free base polymer will remain in free base form both when it is exposed to the high electrolyte concentration (and often the alkaline environment) which prevails in detergent concentrates, and when it is exposed
10 to the lower electrolyte concentration (and possible low alkalinity) which prevails in wash water into which the detergent concentrate has been distributed. The release of the enzyme or other active ingredient from within the matrix cannot therefore be due to formation of a water
15 soluble salt but instead is due to the matrix retaining the active ingredient prior to exposure to wash water but releasing the active ingredient when it is exposed to wash water.

It would be desirable to be able to provide particles
20 having a matrix which provides an improved combination of retention and release of an active ingredient according to whether or not the particles are exposed to a liquid detergent or to the wash water. In particular, it would be desirable to provide an improved matrix which remains
25 sufficiently unswollen while the particles are in liquid detergent prior to exposure to wash water that it retains the active ingredient, but which swells upon contact with wash water so as to allow release of the active ingredient. Further, it would be desirable for such swelling to occur
30 sufficient to stretch or disrupt a polymer shell around the matrix.

According to the invention, a particulate composition comprises particles having a polymeric matrix including a detergency active ingredient, wherein the polymeric matrix
35 is formed of a free base form of a cationic polymer which is a co-polymer of

(a) an ethylenically unsaturated hydrophobic monomer with

(b) a monomer of the formula



where R^1 is hydrogen or methyl, X is O or NH, R^2 is alkylene containing at least two carbon atoms, R^3 is
5 a hydrocarbon group containing at least 4 carbon atoms and R^4 is hydrogen or a hydrocarbon group.

The preferred monomers are those in which R^3 is tertiary butyl since the presence of the tertiary butyl group imposes particularly useful swelling properties on
10 the polymer formed from that monomer. However R^3 may be other butyl or higher alkyl groups or it may be other hydro-carbon groups containing at least 4 carbon atoms (but usually not more than 8 carbon atoms). The t-butyl group is also advantageous because it seems to render the
15 monomer units containing it more resistant to alkaline hydrolysis.

R^4 is frequently hydrogen but it can be alkyl such as methyl, ethyl or higher alkyl or it can be other hydro carbon group. The total number of carbon atoms in R^3 and
20 R^4 together is usually below 12, often below 8.

R^2 is usually ethylene but it can be other linear or branched alkylene group containing two or more (for instance 2-4) carbon atoms.

R^1 is usually methyl.

25 X can be NH, with the result that the cationic monomer is preferably a monoalkyl or dialkyl aminoalkyl (meth) acrylamide monomer, but preferably X is O, with the result that the cationic monomer is preferably a monoalkyl or dialkyl aminoalkyl (meth) acrylate.

30 The hydrophobic monomer can be any ethylenically unsaturated monomer which is insoluble in water, for instance generally having a partition coefficient K between hexane and deionised water at 20°C of at least 5 and preferably at least 10. The hydrophobic monomer can be a
35 water-insoluble alkyl ester of methacrylic acid or other aliphatic, water-insoluble monomer such as methyl, ethyl or butyl acrylate or methacrylate. However the preferred

hydrophobic monomers are ethylenically unsaturated aromatic hydrocarbon monomers, such as styrenes, preferably styrene or a methyl styrene.

5 The amount of the cationic monomer which should be used will depend in part on the active ingredient which is entrapped within the monomer. The proportion of cationic free based monomer should be such that there is little or no release of the active ingredient prior to exposure to the wash water but that there is significant swelling and
10 release of the active ingredient upon exposure to the wash water.

 The degrees of swelling which will result in retention or release of the active ingredient depend in part on the molecular size of the active ingredient, in that good
15 retention of an active ingredient of small molecular size requires that the polymer should be less swollen (when exposed to the detergent concentrate) than when the active ingredient has a higher molecular size. Similarly, good release when exposed to wash water requires a higher degree
20 of swelling for higher molecular size active ingredients than for lower molecular size active ingredients. Generally the amount of cationic monomer will be within the range 5-30 mole % or 10-50 weight %. Best results, especially when the active ingredient is an enzyme, are
25 generally achieved with amounts of from around 12-25 mole % of the cationic free base monomer. When, as is preferred, the free base monomer is t-butylamino-ethyl methacrylate and the hydrophobic monomer is a styrene or methyl styrene, the amount of cationic monomer is
30 preferably from 20%-45% by weight, most preferably around 30%-40% by weight, especially when the active ingredient is a detergent enzyme.

 The matrix can be formed of recurring units of monomers consisting solely of the hydrophobic monomer and
35 the free base cationic monomer but if desired minor amounts of other monomers may be included.

The matrix is preferably formed by a method analogous to that which is described in EP 361677 or EP 356239 for the formation of a matrix of anionic polymer. Thus it may be made by dehydrating particles each of which is an oil-in-water emulsion of the free base polymer or it may be made by forming particles of a salt of the polymer with a volatile acid and evaporating the volatile acid during the drying so as to form the free base of the polymer.

The presence of cationic monomer as acid salt form can significantly increase the swellability, or even the solubility, of the polymer in the detergent concentrate or in the wash water and so preferably the polymer is as free as is reasonably possible of the cationic monomer in the form of water soluble acid salt. For instance the amount of cationic monomer groups in the form of salt, in the polymer, should be as small as possible and should be below 20 mole %, preferably below 10 mole % and most preferably below 5 mole % based on the amount of free base cationic monomer groups in the polymer. Preferably it is substantially zero.

The preferred way of making the particles of polymeric matrix is by forming a reverse phase dispersion in a water immiscible non-aqueous liquid of droplets containing the chosen active ingredient and either an oil-in-water emulsion of the polymer or an aqueous solution of a salt of the polymer with a volatile acid and then distilling the dispersion so as to eliminate the water and, if necessary, to drive off the volatile acid. The formation of the reverse phase dispersion is preferably conducted in the presence of a polymeric (generally amphipathic) stabiliser and/or an emulsifier, for instance as described in EP 356239 and EP 361677 and WO 92/20771.

When, as is preferred, the matrix particles are made by providing a solution of a water soluble salt form of the polymer, this solution can be made by acidifying, using a volatile acid, an oil-in-water emulsion formed by oil-in-water emulsion polymerisation of the monomers. Preferably,

however, the solution is made by polymerising the free base monomer and the hydrophobic monomer while dissolved in an organic solvent so as to form a solution of the free base polymer in organic solvent. This is followed by addition of an aqueous solution of a volatile acid wherein the solvent has higher volatility than the acid. The solvent is then distilled off so as to leave a solution in water of the salt form of the polymer. A suitable volatile acid is acetic acid, in which event a suitable solvent is n-butyl acetate.

In order to maximise the conversion of the salt form of the cationic polymer to the free base form, it is desirable to bake the product, after distilling off the water, at a temperature of at least 95°C and usually 100°C for at least 15 minutes and usually at least 20 or 30 minutes. Preferably this is conducted under sufficient vacuum (if necessary) to maximise the removal of volatile acid.

The active ingredient can be incorporated in the polymeric matrix as a substantially uniform solution or dispersion or it can be distributed non-uniformly.

It can be any active ingredient which can usefully be incorporated into a detergent concentrate and which should preferably be released from the matrix only after dilution of the concentrate into wash water. Accordingly it can be a material such as, for instance, a bleach activator, an optical brightener or a photobleach. Preferably, however, it is a detergent enzyme, that is to say an enzyme that is usefully incorporated into a detergent. It can be, for instance, a lipase, protease, cutinase, amylase, cellulase or oxidoreductase (eg a peroxidase, or an oxidase such as laccase). The invention is of particular value when the liquid detergent is to include a protease and at least one other type of enzyme since by encapsulating the protease, or by encapsulating the or each enzyme other than protease, interaction between the enzymes in the detergent concentrate can be minimised.

A polymeric shell may be formed around the particles of core, for instance by a coacervation technique as described in EP-A-356,239 or WO92/20771 or, preferably, by interfacial condensation as described in, for instance, Application ... filed even date herewith reference PRL03620WO claiming priority from GB 9526707. Preferably the particles have a shell (around the core) of a polyamide or other condensation polymer, preferably formed by interfacial condensation.

The particles that are formed can, depending upon the dispersion conditions and components, be in the form of beads which can be recovered as dry powder, for instance wherein the beads have a dry size of at least 90% by weight above 50 μm and often above 100 μm , for instance up to 1000 μm . Preferably, however, the particles have a smaller size, generally 90% by weight below 30 μm and often below 10 μm or 20 μm down to, for instance, 0.5 μm or less. It is then generally preferred that the particles remain as a substantially stable dispersion in a non-aqueous liquid. Thus, either the particles do not settle out (which is preferred) or any settled particles can easily be redispersed by stirring or shaking.

The initial formation and the subsequent dehydration of the reverse phase dispersion are generally both conducted while the continuous phase of the dispersion is a hydrocarbon non-aqueous liquid, but various other non-aqueous liquids which are known to be suitable for reverse phase dispersions can be used. Although the final product can be added direct to a detergent concentrate, it is preferred to provide the particles as a dispersion in a water miscible liquid, generally a non-ionic surfactant as described in WO 94/25560 to which reference should be made for description of suitable materials, amounts and methods. The amount of particles in such a dispersion is usually above 10% by weight of the dispersion.

The particles may be dispersed in a liquid detergent, for instance by blending a dispersion of particles (usually

after dehydration) in a surfactant or in another water-immiscible liquid or in an water-immiscible liquid into the liquid detergent.

The liquid detergent containing the particles may be aqueous, typically containing up to 70% water and 0-30% organic solvent, or non-aqueous.

The detergent composition comprises one or more surfactants, each of which may be anionic, non-ionic, cationic, or zwitterionic. The detergent will usually contain 0-50% of anionic surfactant such as linear alkylbenzenesulfonate (LAS), alpha-olefinsulfonate (AOS), alkyl sulfate (fatty alcohol sulfate) (AS), alcohol ethoxysulfate (AEOS or AES), secondary alkanesulfonates (SAS), alpha-sulfo fatty acid methyl esters, alkyl- or alkenylsuccinic acid, or soap. It may also contain 0-40% of non-ionic surfactant such as alcohol ethoxylate (AEO or AE), carboxylated alcohol ethoxylates, nonylphenol ethoxylate, alkylpolyglycoside, alkyl dimethylamine oxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, or polyhydroxy alkyl fatty acid amide (e.g. as described in WO 92/06154).

The detergent, if built, may contain 1-65% of a detergent builder or complexing agent such as zeolite, diphosphate, triphosphate, phosphonate, citrate, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTMPA), alkyl- or alkenylsuccinic acid, soluble silicates or layered silicates (e.g. SKS-6 from Hoechst). The detergent may also be unbuilt, i.e. essentially free of detergent builder.

The detergent may comprise one or more polymers. Examples are carboxymethylcellulose (CMC), poly(vinylpyrrolidone) (PVP), polyethyleneglycol (PEG), poly(vinyl alcohol) (PVA), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

The detergent may contain a bleaching system which may comprise a H_2O_2 source such as perborate or percarbonate which may be combined with a peracid-forming bleach activator such as tetraacetylenediamine (TAED) or
5 nonanoyloxybenzenesulfonate (NOBS). Alternatively, the bleaching system may comprise peroxyacids of, e.g., the amide, imide, or sulfone type.

The enzymes of the detergent composition of the invention may be stabilized using conventional stabilizing
10 agents, e.g. a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative such as, e.g., an aromatic borate ester, and the composition may be formulated as described in, e.g., WO 92/19709 and WO 92/19708. The stabiliser may
15 be incorporated in the capsules (generally in the core) or may be in the liquid phase, especially when there is enzyme in the liquid phase.

The detergent may also contain other conventional detergent ingredients such as, e.g., fabric conditioners
20 including clays, foam boosters, suds suppressors, anti-corrosion agents, soil-suspending agents, anti-soil-redeposition agents, dyes, bactericides, optical brighteners, or perfume.

The pH (measured in aqueous solution at use concentration) will usually be neutral or alkaline, e.g. in
25 the range of 7-11.

Particular forms of detergent compositions in which the novel particles can be dispersed include:

30

1) An aqueous liquid detergent composition comprising

	Linear alkylbenzenesulfonate (calculated as acid)	15	- 21%
5	Alcohol ethoxylate (e.g. C ₁₂₋₁₅ alcohol, 7 EO or C ₁₂₋₁₅ alcohol, 5 EO)	12	- 18%
	Soap as fatty acid (e.g. oleic acid)	3	- 13%
	Alkenylsuccinic acid (C ₁₂₋₁₄)	0	- 13%
10	Aminoethanol	8	- 18%
	Citric acid	2	- 8%
	Phosphonate	0	- 3%
	Polymers (e.g. PVP, PEG)	0	- 3%
	Borate (as B ₂ O ₇)	0	- 2%
15	Ethanol	0	- 3%
	Propylene glycol	8	- 14%
	Enzymes (calculated as pure enzyme protein)	0.0001	- 0.1%
20	Minor ingredients (e.g. dispersants, suds suppressors, perfume, optical brightener)	0	- 5%

2) An aqueous structured liquid detergent composition comprising

	Linear alkylbenzenesulfonate (calculated as acid)	15	- 21%
5	Alcohol ethoxylate (e.g. C ₁₂₋₁₅ alcohol, 7 EO, or C ₁₂₋₁₅ alcohol, 5 EO)	3	- 9%
	Soap as fatty acid (e.g. oleic acid)	3	- 10%
10	Zeolite (as NaAlSiO ₄)	14	- 22%
	Potassium citrate	9	- 18%
	Borate (as B ₄ O ₇)	0	- 2%
	Carboxymethylcellulose	0	- 2%
	Polymers (e.g. PEG, PVP)	0	- 3%
15	Anchoring polymers such as, e.g., lauryl methacrylate/acrylic acid copolymer; molar ratio 25:1; MW 3800	0	- 3%
	Glycerol	0	- 5%
20	Enzymes (calculated as pure enzyme protein)	0.0001	- 0.1%
	Minor ingredients (e.g. dispersants, suds suppressors, perfume, optical brighteners)	0	- 5%

25

3) An aqueous liquid detergent composition comprising

	Linear alkylbenzenesulfonate (calculated as acid)	15	- 23%
5	Alcohol ethoxysulfate (e.g. C ₁₂₋₁₅ alcohol, 2-3 EO)	8	- 15%
	Alcohol ethoxylate (e.g. C ₁₂₋₁₅ al- cohol, 7 EO, or C ₁₂₋₁₅ alcohol, 5 EO)	3	- 9%
10	Soap as fatty acid (e.g. lauric acid)	0	- 3%
	Aminoethanol	1	- 5%
	Sodium citrate	5	- 10%
	Hydrotrope (e.g. sodium toluenesulfonate)	2	- 6%
15	Borate (as B ₂ O ₃)	0	- 2%
	Carboxymethylcellulose	0	- 1%
	Ethanol	1	- 3%
	Propylene glycol	2	- 5%
20	Enzymes (calculated as pure enzyme protein)	0.0001	- 0.1%
	Minor ingredients (e.g. polymers, dispersants, perfume, optical brighteners)	0	- 5%

4) An aqueous liquid detergent composition comprising

	Linear alkylbenzenesulfonate (calculated as acid)	20	- 32%
5	Alcohol ethoxylate (e.g. C ₁₂₋₁₅ alcohol, 7 EO, or C ₁₂₋₁₅ alcohol, 5 EO)	6	- 12%
	Aminoethanol	2	- 6%
	Citric acid	8	- 14%
	Borate (as B ₂ O ₃)	1	- 3%
10	Polymer (e.g. maleic/acrylic acid copolymer, anchoring polymer such as, e.g., lauryl methacrylate/acrylic acid copolymer)	0	- 3%
15	Glycerol	3	- 8%
	Enzymes (calculated as pure enzyme protein)	0.0001	- 0.1%
20	Minor ingredients (e.g. hydro- tropes, dispersants, perfume, optical brighteners)	0	- 5%

5) LIQUID DISHWASHING COMPOSITION WITH CLEANING
SURFACTANT SYSTEM

	Non-ionic surfactant	0	-	1.5%
5	Octadecyl dimethylamine N-oxide dihydrate	0	-	5%
	80:20 wt.C18/C16 blend of octadecyl dimethylamine N-oxide dihydrate and hexadecyldimethyl amine N-oxide dihydrate	0	-	4%
10	70:30 wt.C18/C16 blend of octadecyl bis (hydroxyethyl)amine N-oxide anhydrous and hexadecyl bis (hydroxyethyl)amine N-oxide anhydrous	0	-	5%
15	C ₁₃ -C ₁₅ alkyl ethoxysulfate with an average degree of ethoxylation of 3	0	-	10%
	C ₁₂ -C ₁₅ alkyl ethoxysulfate with an average degree of ethoxylation of 3	0	-	5%
20	C ₁₃ -C ₁₅ ethoxylated alcohol with an average degree of ethoxylation of 12	0	-	5%
	A blend of C ₁₂ -C ₁₅ ethoxylated alcohols with an average degree of ethoxylation of 9	0	-	6.5%
25	A blend of C ₁₃ -C ₁₅ ethoxylated alcohols with an average degree of ethoxylation of 30	0	-	4%
	Sodium disilicate	0	-	33%
	Sodium tripolyphosphate	0	-	46%
30	Sodium citrate	0	-	28%
	Citric acid	0	-	29%

5	Sodium carbonate	0	- 20%
	Sodium perborate monohydrate	0	- 11.5%
	Tetraacetyl ethylene diamine (TAED)	0	- 4%
	Maleic acid/acrylic acid copolymer	0	- 7.5%
	Sodium sulphate	0	- 12.5%
	Enzymes	0.0001	- 0.1%

6) NON-AQUEOUS LIQUID AUTOMATIC DISHWASHING COMPOSITION

10	Liquid nonionic surfactant (e.g. alcohol ethoxylates)	2.0	- 10.0%
	Alkali metal silicate	3.0	- 15.0%
	Alkali metal phosphate	20.0	- 40.0%
15	Liquid carrier selected from higher glycols, polyglycols, polyoxides, glycolethers	25.0	- 45.0%
	Stabilizer (e.g. a partial ester of phosphoric acid and a C ₁₆ -C ₁₈ alkanol)	0.5	- 7.0%
	Foam suppressor (e.g. silicone)	0	- 1.5%
20	Enzymes	0.0001	- 0.1%

7) NON-AQUEOUS LIQUID DISHWASHING COMPOSITION

5	Liquid nonionic surfactant (e.g. alcohol ethoxylates)	2.0	- 10.0%
	Sodium silicate	3.0	- 15.0%
	Alkali metal carbonate	7.0	- 20.0%
	Sodium citrate	0.0	- 1.5%
10	Stabilizing system (e.g. mixtures of finely divided silicone and low molecular weight dialkyl polyglycol ethers)	0.5	- 7.0%
	Low molecule weight polyacrylate polymer	5.0	- 15.0%
	Clay gel thickener (e.g. bentonite)	0.0	- 10.0%
	Hydroxypropyl cellulose polymer	0.0	- 0.6%
15	Enzymes	0.0001	- 0.1%
	Liquid carrier selected from higher lycols, polyglycols, polyoxides and glycol ethers	Balance	

8) THIXOTROPIC LIQUID AUTOMATIC DISHWASHING COMPOSITION

	C ₁₂ -C ₁₄ fatty acid	0	-	0.5%
	Block co-polymer surfactant	1.5	-	15.0%
	Sodium citrate	0	-	12%
5	Sodium tripolyphosphate	0	-	15%
	Sodium carbonate	0	-	8%
	Aluminium tristearate	0	-	0.1%
	Sodium cumene sulphonate	0	-	1.7%
	Polyacrylate thickener	1.32	-	2.5%
10	Sodium polyacrylate	2.4	-	6.0%
	Boric acid	0	-	4.0%
	Sodium formate	0	-	0.45%
	Calcium formate	0	-	0.2%
15	Sodium n-decyldiphenyl oxide disulphonate	0	-	4.0%
	Monoethanol amine (MEA)	0	-	1.86%
	Sodium hydroxide (50%)	1.9	-	9.3%
	1,2-Propanediol	0	-	9.4%
	Enzymes	0.0001	-	0.1%
20	Suds suppressor, dye, perfumes, water	Balance		

9) LIQUID AUTOMATIC DISHWASHING COMPOSITION

5	Alcohol ethoxylate	0	- 20%
	Fatty acid ester sulphonate	0	- 30%
	Sodium dodecyl sulphate	0	- 20%
	Alkyl polyglycoside	0	- 21%
	Oleic acid	0	- 10%
10	Sodium disilicate monohydrate	18	- 33%
	Sodium citrate dihydrate	18	- 33%
	Sodium stearate	0	- 2.5%
	Sodium perborate monohydrate	0	- 13%
	Tetraacetyl ethylene diamine (TAED)	0	- 8%
	Maleic acid/acrylic acid copolymer	4	- 8%
	Enzymes	0.0001	- 0.1%

15 10) LIQUID AUTOMATIC DISHWASHING COMPOSITION CONTAINING PROTECTED BLEACH PARTICLES

20	Sodium silicate	5	- 10%
	Tetrapotassium pyrophosphate	15	- 25%
	Sodium triphosphate	0	- 2%
	Potassium carbonate	4	- 8%
	Protected bleach particles, e.g. chlorine	5	- 10%
25	Polymeric thickener	0.7	- 1.5%
	Potassium hydroxide	0	- 2%
	Enzymes	0.0001	- 0.1%
	Water	Balance	

- 11) Detergent formulations as described above in 1-4 wherein all or part of the linear alkylbenzenesulfonate is replaced by (C₁₂₋₁₈) alkyl sulfate.
- 12) Detergent formulations as described above in 1-5 which contain a stabilised or encapsulated peracid, either as an additional component or as a substitute for already specified bleach systems.
- 13) Detergent composition formulated as a non-aqueous detergent liquid comprising a liquid nonionic surfactant such as, e.g., linear alkoxylated primary alcohol, a builder system (e.g. phosphate), enzyme and alkali. The detergent may also comprise anionic surfactant and/or a bleach system.
- 14) Automatic dishwashing compositions as described in 5) and 9), wherein perborate is replaced by percarbonate.
- 15) Automatic dishwashing compositions as described in 5) and 9) which additionally contain a manganese catalyst. The manganese catalyst may, e.g., be one of the compounds described in "Efficient manganese catalysts for low-temperature bleaching", Nature 369, 1994, pp. 637-639.

The amount of the or each enzyme in the liquid detergent typically corresponds to an amount of 0.0001 to 1mg pure enzyme protein per litre of wash liquor.

The following are examples of the invention:

25. Example 1

A co-polymer of about 65% by weight styrene and 45% by weight t-butyl amino ethyl methacrylate is synthesized by isothermal solution polymerisation in n-butyl acetate using t-butyl perbenzoate as initiator. Aqueous acidic acid solution is then added to the organic solution and the butyl acetate was distilled off, leaving a 20%-30% weight solution of the co-polymer, as the acetate salt, in water at pH 4-5.5.

Example 2

35 The solution of Example 1 is mixed with a liquid Savinase (Trademark) preparation and dispersed in hydrocarbon oil, with adjustment of the pH to 4.5, followed

by distillation to produce a dried dispersion all substantially as described in Example 2 of WO 92/20771. The dispersion is then held at 100°C for 30 minutes under vacuum to drive off acetic acid.

5 The particles produced in this Example are added to a typical European liquid detergent formulations at 0.10 KNPu/g proteolytic enzyme activity. The detergent sample is subjected to a storage test at the end of which 86% of the original enzyme activity is released into wash water
10 and only 15% of the original enzyme activity had escaped into the liquid phase prior to the dilution with wash water.

 These results clearly demonstrate that the majority of the enzyme remains entrapped within the polymer matrix
15 particles under detergent storage and releases the enzyme under wash conditions.

Example 3

 This example shows that non-proteolytic enzymes such as Lipolase, a lipase enzyme can be protected from the
20 degrading protease such as Savinase enzyme by use of product formed in Example 2.

 A concentrated liquid detergent containing liquid Lipolase enzyme at 1.0 KLU/g lipolytic enzyme activity is dosed with either Savinase particles of Example 2 or with
25 liquid Savinase enzyme at 0.10 KNPu/g protease enzyme activity. Each detergent sample is subjected to an accelerated storage test for 3 and 7 days.

 After performing the above storage test, the respective detergent samples are analysed for lipolytic
30 enzyme activity.

 The percentage of lipolytic enzyme activity remaining after 3 and 7 days in detergent samples are given in Table 1.

Table 1

Savinase Enzyme Form	% Lipolase remaining after 3 days	% Lipolase remaining after 7 days
Particles of Ex 2	70	45
Normal liquid	10	3

These results clearly show that encapsulation of the protease within the capsules of Example 2 protects the lipolase from the deactivation, compared to the corresponding detergent where the protease is not entrapped within the particles.

Example 4

The process of Example 2 is repeated except that Lipolase is included in the particles instead of Savinase.

The particles of this Example are added to a typical European liquid detergent compositions at 1.0 KLU/g lipolytic enzyme activity. The resulting detergent sample is subjected to a storage test at the end of which 6% of the original enzyme activity is in the liquid phase and 69% of the original enzyme activity is released upon dilution into wash liquor.

Example 5

A concentrated liquid detergent containing liquid Savinase enzyme at 0.10 KNPu/g enzyme activity is dosed with either Lipolase particles of Example 5 or with liquid Lipolase enzyme at 1.0 KLU/g enzyme activity. The respective detergent samples are placed under accelerated storage test at 30°C for 7 days.

After carrying out the above storage test, the samples are subjected to lipolytic enzyme activity determination. The amount of lipase activity remaining after the test is given in Table 2.

Concurrently, the above test is performed is liquid detergent containing no liquid Savinase enzyme.

Table 2

Lipolase Enzyme Form	% Lipolase remaining in absence of Savinase	% Lipolase remaining in presence of Savinase
Particles of Ex 4	56	46
Normal Liquid	70	0

Example 6

The process of Examples 1-5 is repeated using different co-polymers. When the amount of the free base cationic monomer is increased above 40% by weight there is increased leakage of the Savinase, leading to reduced Lipolase activity in the test system of Example 3. When the amount of cationic monomer is reduced significantly below 30%, there is reduced proteolytic activity upon addition to wash water, indicating inferior release of the enzyme.

When the butyl amino-ethyl methacrylate free base is replaced by dimethyl amino-ethyl methacrylate or dimethyl amino-ethyl methacrylate, there is increased leakage of the protease into the detergent concentrate with consequential reduction in the lipolase activity in Example 3.

CLAIMS

1. A particulate composition comprising particles having a polymeric matrix including a detergency active ingredient and wherein the polymeric matrix is formed of a co-polymer
5 of (a) an ethylenically unsaturated hydrophobic monomer with (b) a free base monomer of the formula
- $$\text{CH}^2 = \text{CR}^1\text{COXR}^2\text{NR}^3\text{R}^4$$
- where R is hydrogen or methyl, R² is alkylene containing at least two carbon atoms, X is O or NH, R³ is
10 a hydrocarbon group containing at least 4 carbon atoms and R⁴ is hydrogen or a hydrocarbon group.
2. A composition according to Claim 1 in which R³ is t-butyl and R⁴ is hydrogen.
3. A composition according to Claim 1 or Claim 2 in which
15 R¹ is methyl, R² is ethylene and X is O.
4. A composition according to any preceding claim in which the hydrophobic monomer is a styrene.
5. A composition according to Claim 1 wherein the polymer is a co-polymer of 55-80 weight % of styrene or methyl
20 styrene with 20%-45% by weight t-butylamino-ethyl methacrylate.
6. A composition according to any preceding claim in which there is a polymeric shell around the matrix.
7. A composition according to claim 6 in which the shell
25 is formed of a polyamide or other condensation polymer.
8. A dispersion according to any preceding claim in which the active ingredient is detergent enzyme.
9. A composition according to any preceding claim in which the particles are 90% by weight below 30µm.
- 30 10. A composition according to Claim 9 and which is a dispersion of at least 10% by weight of the particles in a liquid selected from water immiscible liquids, surfactants and other water miscible liquids.
11. A composition according to claim 9 and which is a
35 dispersion of the particles in a detergent concentrate.
12. A composition according to claim 11 and which is a liquid detergent concentrate in which the particles are

dispersed and wherein the active ingredient in the particles is a first enzyme and the detergent also includes a second enzyme, wherein de-activation of the first enzyme by the second enzyme or vice versa is substantially
5 prevented in the concentrate by the retention of the first enzyme within the particles and wherein the first enzyme is released upon dilution of the concentrate into wash water.

INTERNATIONAL SEARCH REPORT

International Application No
PC 1/GB 96/03232

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J13/16 C11D17/00 C11D3/37 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 8612 Derwent Publications Ltd., London, GB; Class A14, AN 86-079085 XP002029165 & JP 61 028 441 A (LION CORP) , 8 February 1986 see abstract	1-3,8
A	--- EP 0 356 239 A (ALLIED COLLOIDS LTD) 28 February 1990 cited in the application see claims 1-10	1,6,8
A	--- WO 92 20771 A (ALLIED COLLOIDS LTD) 26 November 1992 cited in the application see examples 2,4,5 -----	1,6,8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

9 April 1997

Date of mailing of the international search report

23. 04. 97

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